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Novel method of preparation of C/Sn-SnO₂ nanocomposite Li-ion anode material derived from plant polysaccharides

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Abstract

C/Sn-SnO₂ nanocomposite was obtained in one step pyrolysis and carboreduction process, providing formation of tin-based nanograins encapsulated in carbon buffer matrix derived from plant polysaccharide (potato starch). Electrical conductivity of the obtained material was carried out within temperature range -20÷40 °C. Cyclic voltammetry (CV) and charge-discharge tests were performed in Li/Li⁺/(C/Sn-SnO₂) R2032-type coin cells within 0.02÷1.5 V potential range. Furthermore, electrochemical impedance spectroscopy (EIS) was used to characterize electrochemical properties of the nanocomposite. The C/Sn-SnO₂ anode material provided at least 538 mAh g⁻¹ at C/20-rate and revealed good coulombic efficiency and capacity retention in charge-discharge cell tests.

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1. Introduction

Graphite and its derivatives are used as anode materials in commercial Li-ion rechargeable batteries, mainly due to the good electrochemical properties and low cost of production. The progress of technology shows that the currently used batteries based on graphite anodes do not have appropriate, required operating parameters, assigned to their low capacity (~370 mAh g⁻¹) [1]. Tin has been shown as one of the best options for replacing present anode materials as a result of its high theoretical capacity (~994 mAh g⁻¹) [2]. The formation of Li_xSn_y alloys is

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accompanied by cyclic changes of elementary cell volume, reaching up to 300% [2] which lead to loss of electrical contact between active material and current collector as well as physical damage of the cell caused by high strains. One of the ways to reduce tin volume changes involved downsizing of the material particles, however, it was found that the cycling stability of nano-Sn particles was insufficient [3]. Over the last decade most of the studies were focused on designing composites containing Sn and a stress-accommodating phase [4-9], nevertheless, the multi-step processes used to synthesis of such composites are complex and expensive [10].

The goal of presented work is to develop a novel method of preparation of nanocomposite anode material, in which nanometric tin-based grains will be encapsulated in a flexible carbon buffer matrix derived from plant polysaccharides, in a simple and inexpensive process basing on the idea proposed by Molenda [11].

2. Experimental

Tin precursor for C/Sn-SnO₂ nanocomposite material was prepared using a modified reverse microemulsion method (w/o), which allowed controlling size and shape of the obtained SnO₂ particles. Then, SnO₂ nanoparticles were coated by a plant polysaccharide (potato starch) based carbon precursor in gelatinization process. The resulting PS/SnO₂ precursor was pyrolysed under Ar flow (purity 99.999%, 10 dm³ h⁻¹) at 700 °C for 6 h. Pyrolysis and carboreduction process led to formation of C/Sn-SnO₂ nanocomposite in which tin-based nanograins were encapsulated in carbon buffer matrix.

Optimal conditions of the pyrolysis were determined by thermal gravimetric analysis (TGA) coupled with mass spectrometry of evolved gases (MS-EGA). TGA studies were performed in a Mettler-Toledo 851^e thermo-analyser using 150 µL corundum crucibles under flow of air or argon (80 mL min⁻¹), within temperature range 30÷1000 °C and heating rate 10 °C min⁻¹. The simultaneous MS-EGA was performed using on-line joined quadrupole mass spectrometer (QMS) Thermostar (Balzers). The carbon content in the composite was determined by the temperature programmed oxidation (TPO). The crystal structure of C/Sn-SnO₂ nanocomposite was characterized by an X-ray diffraction (XRD) using D2 PHASER Bruker diffractometer equipped with a graphite monochromator using Cu Kα1 radiation. Electrical conductivity measurement of the composite was performed using AC 4-probe method within temperature range -20÷40 °C. The fine powder sample was placed into a glass tube and pressed by a screw-press between parallel gold disc electrodes (Ø = 5 mm) till the measured resistance remained constant. Obtained material was used to cells assembling in an argon-filled glove box. The electrolyte consisted of a solution of 1M LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with EC/DEC volume ratio of 1:1. Li/Li⁺/(C/Sn-SnO₂) R2032-type coin cells were tested at a constant current density in the voltage range of 0.02÷1.5 V at room temperature using ATLAS 0961 MBI multichannel battery testing system. Assembled batteries were tested in the C/20 and C/10 current rates. The battery charging at rate of C/20 will deliver its nominal evaluated capacity in 20 h, C/10-rate should provide its nominal capacity in 10 h respectively. Cyclic voltammetry measurements (CV) were carried out on PGSTAT302N galvanostat/potentiostat over the potential range 0.02÷1.5 V vs. Li/Li⁺ with scanning rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage of 1 mV over the frequency range from 0.01 Hz to 100 kHz.

3. Results

The real carbon content in the obtained composite determined by TPO method was 37 wt.% (Fig.1).

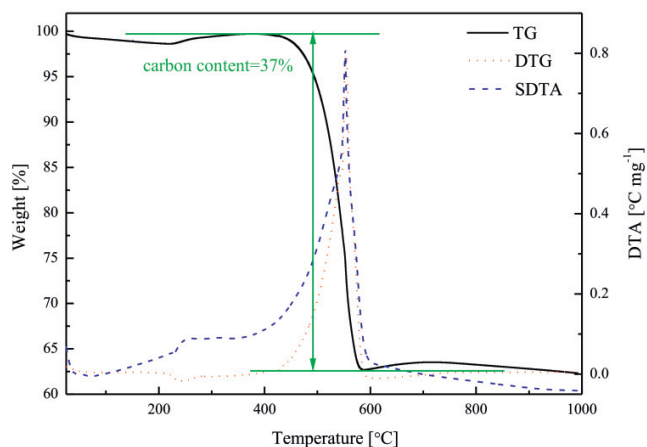


Fig. 1. Determination of carbon content in C/Sn-SnO₂ by TPO method.

The XRD pattern of the C/Sn-SnO₂ composite is shown in Fig. 2. Part of the observed diffraction reflexes can be assigned to β -Sn phase with the space group $I4_1/amd$ (PDF-4 file #00-004-0673). SnO₂ phase with the space group $P4_2/mnm$ (PDF-4 file #00-041-1445) can also be identified in the sample. Lack of significant reflexes related to carbon material suggests that carbon buffer matrix was amorphous. The crystallite sizes calculated from the Debye–Scherrer formula were about 43 nm for β -Sn phase and 44 nm for SnO₂ phase. The obtained C/Sn-SnO₂ composite revealed high electrical conductivity at room temperature as well as low activation energy of electrical conductivity (Fig. 3). Values of the activation energy of the ac conductivity were calculated in the $-20 \div 40$ °C temperature range.

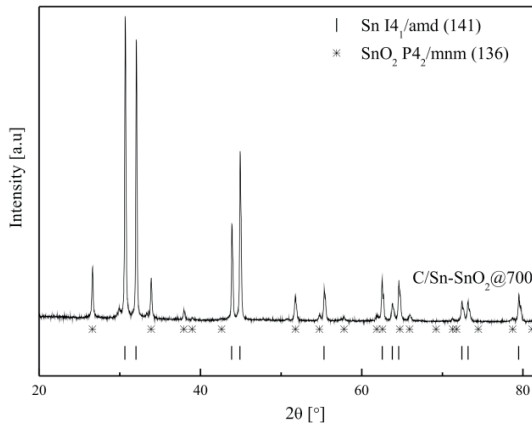


Fig. 2. X-ray powder diffraction pattern for C/Sn-SnO₂ composite.

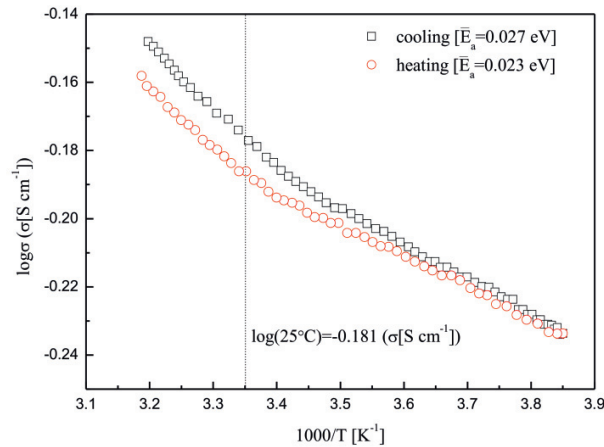


Fig. 3. Electrical conductivity of C/Sn-SnO₂ composite.

Measurements of cyclic voltammetry, impedance spectroscopy and charge-discharge tests were carried out in Li/Li⁺/(C/Sn-SnO₂) R2032-type coin cells. Loading of active material (Sn-SnO₂) in the assembled cells was about 6.8 mg. The CV measurement for Li/Li⁺/(C/Sn-SnO₂) cell was collected during the first three cycles (Fig. 4). In the cathodic polarization process, two small humps, seen in the potential range of 0.2÷0.6 V, are attributed to Li_xSn_y alloy formation. On the anodic branch of the curve the current increase with plateau at 0.45 V is recorded followed multiple distinct peaks at 0.65, 0.75 and 0.85 V, which originate from the delithiation of Li_xSn_y alloy phases [12].

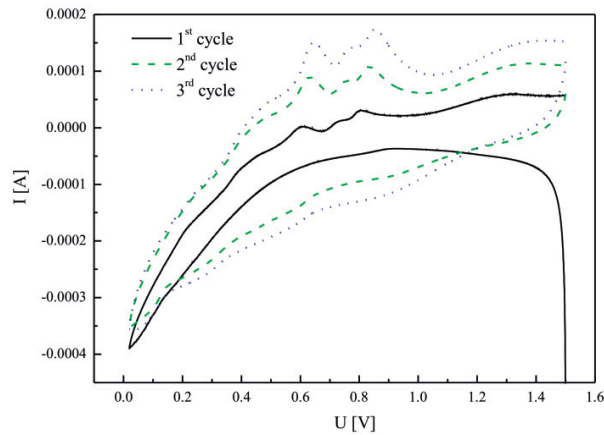


Fig. 4. CV curves of Li/Li⁺/(C/Sn-SnO₂) cell at 0.1 mV s⁻¹ scanning rate.

The charge-discharge tests for the Li/Li⁺/(C/Sn-SnO₂) cells are presented in Fig. 5. The initial charge capacity was found to be 660 mAh g⁻¹ (C/20-rate). During first cycle very large irreversible capacity was related to formation of SEI layer on electrode surface and also reduction of SnO₂. Furthermore, carbon buffer matrix which is not yet optimized may not effectively prevent the volume change of the active material during the intercalation process. The reversible capacity after tenth charge-discharge cycle was 538 mAh g⁻¹ at C/20-rate and coulombic efficiency was 93%. During first charge step at C/10-rate almost two fold decrease in capacity compared to the cell tested at C/20-rate was observed. After tenth charge step the reversible capacity was 429 mAh g⁻¹ at C/10-rate and coulombic efficiency was 94%.

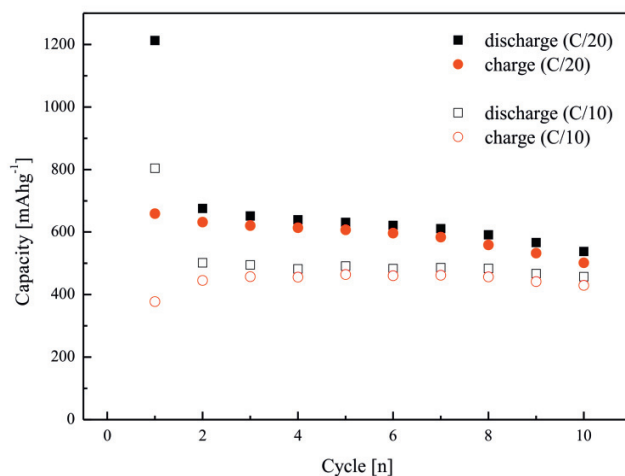


Fig. 5. Charge-discharge capacity of C/Sn-SnO₂ anode composite as function of the cycle number at C/10 and C/20 current rate.

Fig. 6 shows the comparison of EIS spectra for Li/Li⁺/(C/Sn-SnO₂) cell before cycling and after performing ten cycles. The Nyquist plots are represented by a two semicircles in the high and medium frequency range and a straight line at low frequencies. The experimental data were fitted using an equivalent circuit presented in Fig. 6. In the Nyquist plots semicircle in high frequency (R_f) is related to conduction through SEI in carbon matrix, semicircle in the middle frequency (R_{ct}) is connected to interfacial charge transfer and inclined line in low frequency is associated with the diffusion toward a blocking electrode [13]. Determined values of resistance from equivalent circuit from EIS spectra analysis are also presented in Fig. 6. Resistance (R_Ω) related to electrolyte and electrical contact slightly increases with cycle's number suggesting some instability and side reactions. After performing ten cycles R_f significantly decreases what can be connected to formation of easy ion paths through carbon buffer matrix and suggests an optimal SEI formation. Small decrease of R_{ct} after cell cycling (10 cycles) suggests high stability in interfacial charge transfer process.

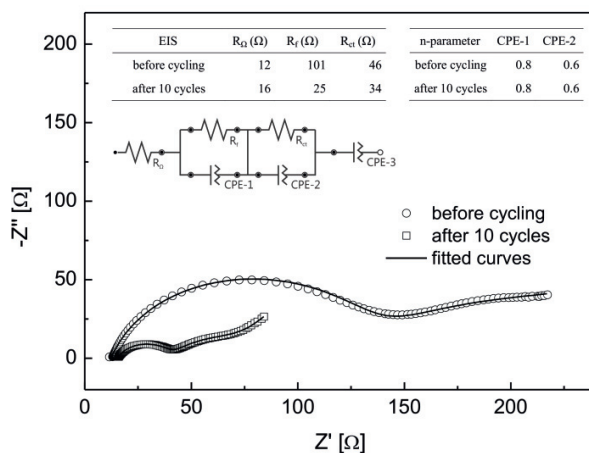


Fig. 6. Nyquist plots of C/Sn-SnO₂ anode composite and corresponding equivalent circuit.

4. Conclusion

The C/Sn-SnO₂ anode material was successfully prepared in one step pyrolysis and carboreduction process of nanometric tin oxide(IV). As a source of carbon plant polysaccharide – potato starch was used. The developed method is easy to further optimization and suitable for tailoring of nanocomposite preparation. Despite the fact that the carbon buffer matrix is not yet sufficiently optimized the obtained composites provided at least 538 mAh g⁻¹ at C/20-rate and revealed good coulombic efficiency and capacity retention in charge-discharge cell tests.

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